NASA CR-66360
RITU 1967-10

CONTRACT NUMBER NAS1-4849

FINAL REPORT

"STUDY OF METHODS OF ENHANCING THE VISIBILITY OF ROCKET SMOKE TRAILS"

RESEARCH INSTITUTE

FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LANGLEY RESEARCH CENTER
LANGLEY STATION
HAMPTON, VIRGINIA 23365

MAY 15, 1967

W. J. MURPHY AND C. S. STOKES

THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY
4150 HENRY AVENUE
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FOREWARD

This final report covers the work sponsored by the Langley Research Center, National Aeronautics and Space Administration, Langley Station, Hampton, Virginia under Contract NAS1-4849.

The work on this project was performed at the Research Institute of Temple University's High Temperature Test Site, Elverson, Pennsylvania. Contributing staff members were: W. J. Murphy, C. S. Stokes, E. W. Smith, L. A. Streng and R. W. Segletes.

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INTRODUCTION

The Research Institute of Temple University carried out the research reported here under sponsorship of the NASA Langley Research Center. The purpose of this research was to attempt to find ways of coloring "smoke" trails produced by hygroscopic agents. Smoke trails are used at Langley to determine wind velocity by photographing the movement of trails laid by ascending rockets. They are also used in other programs for optical acquisition and tracking of vehicles and payloads, and to form a background for photographing atmospheric refraction in blast wave studies.

In these programs "smoke" trails are produced by expelling atomized titanium tetrachloride or other hygroscopic agents into the atmosphere. The titanium tetrachloride reacts with atmospheric water vapor to form droplets of hydrochloric acid and oxides of titanium. Trails made up of these small droplets appear white, and furnish excellent contrast against a clear blue sky. However, against cloud background or haze the contrast of white trails is very poor. For all but very dense haze the contrast can be greatly improved by use of yellow or red filters. If the smoke itself could be colored, the contrast would be improved even with dense haze or cloud background. Colored oil smokes and colored pyrotechnic smokes require much greater payload weight to produce a given volume of smoke. Thus the usefulness of smoke trails would be greatly enhanced if the more efficient hygroscopic trails could be colored.

In general, three different approaches were made to the problem of colored smokes:

(1) addition of various types of coloring agents (dyes or inorganic coloring agents)

(2) reaction of $TiCl_4$ with an organic compound. This reaction was external and in itself a smoke producer.

(3) reactions involving $POCl_3$ and PCl_3

ADDITION OF COLORING AGENTS

A survey of commercially available dye types was made to determine which dyes might be used in coloring a smoke trail. In addition to the use of organic dyeing materials, inorganic coloring agents were tested. These approaches were not successful.

Over one hundred dye types supplied by cooperating dye producing companies were tested. Testing of dyes was divided into two phases. The first phase involved testing the dyes for solubility in $TiCl_4$. The second phase was the actual testing of the $TiCl_4$-dye solution to determine coloring effects in a smoke cloud.

Several chemical companies were contacted directly for dye samples. The majority of dyes tested were not soluble in $TiCl_4$. Those that showed some solubility were tested in Phase II for smoke coloration. This test consisted of spraying approximately 100 cc of $TiCl_4$-dye solution into the atmosphere. In no case did a dye solution of $TiCl_4$ give adequate coloring. In the case of dyes not soluble in $TiCl_4$, the dye was dissolved in the proper solvent, water or alcohol, etc., and the two streams, $TiCl_4$ and dye solution, were sprayed into each other. A faint color could be seen due to the colored solution in the first one to two inches before reaction, but the smoke appeared white.

In addition to the dye studies, red iron oxide (Fe_2O_3) was considered as a coloring agent.

Fe_2O_3 proved to be slightly soluble in $TiCl_4$, forming a reddish brown solution. On spray discharge to the atmosphere, the $TiCl_4$

traveled about six inches before reacting. This was in contrast to the usual one or two inches of travel as in the case of the dye solution. The brown color was visible in the liquid but disappeared in the white smoke.

Attempts were made to produce free iodine in the smoke by addition of KI water solution and NaI water solution to $TiCl_4$.

During preliminary testing in an indoor hood, the water solution was poured into $TiCl_4$. It reacted with its usual violence. After three to five seconds a large reddish brown cake was formed, consisting of "foamed" TiO_2 colored by free iodine.

The water solutions were then sprayed into $TiCl_4$ through a swirlcup injector outdoors. The resulting cloud was not colored although a reddish brown color did appear at the discharge point for a short time (one second or less) during the discharge. Dyes are listed in Tables I and II.

TABLE 1

DYE	SOURCE
Violet VTS	Dynamic Colors
Altocryl Brilliant Red BB	Althouse Chemical
Altocryl Brilliant Red 2R	Althouse Chemical
Supernylite Brilliant Green B	Althouse Chemical
Cekryl Yellow RFC	Althouse Chemical
Nylanthrine Orange SLF	Althouse Chemical
Supernylite Scarlet AFJ	Althouse Chemical
Altocryl Pink 3 GF	Althouse Chemical
Cekryl Red BB	Althouse Chemical
Nydye Yellow S	Althouse Chemical
Azoanthrene Royal Blue S Conc.	Althouse Chemical
Azoanthrene Black WAN	Althouse Chemical
Azoanthrene Black NV	Althouse Chemical
Discharge Fast Yellow DLW	Althouse Chemical
Sol-Aqua-Fast Red 2BL	Althouse Chemical
Experimental Turquoise SW9304	Althouse Chemical
FD&C Yellow No. 6	Althouse Chemical
FD&C Red No. 3	Althouse Chemical
FD&C Yellow No. 5	Althouse Chemical

TABLE 1 (continued)

DYE	SOURCE
Amaplast AAP	American Aniline Products
Amaplast Pink FFT	American Aniline Products
Ortho Nitroaniline Lot 752	American Aniline Products
1, 2 Dihydroxyanthraquinone	American Aniline Products
3, 3'4, 4' Tetraminobiphenyl Lot 1936	American Aniline Products
Ortho Phenylenidiamine	American Aniline Products
1 Aminoanthraquinane Lot 847-848	American Aniline Products
Pylakrome Red LX 1903	Pylam Products
Pylam Pink LX-1700	Pylam Products
Pylam Rose Pink LX-1800	Pylam Products
Methylene Blue SP	Allied Chemical-National Aniline
Rhodamine B Conc. 500%	Allied Chemical-National Aniline
Fast Wool Yellow 3 GL Con. 125%	Allied Chemical-National Aniline
Spirit Soluble Fast Yellow 3G	Allied Chemical-National Aniline
Phospine GN Conc.	Allied Chemical-National Aniline
Rhodomine B Soln.	Allied Chemical-National Aniline
Sandoz Aluminum Blue	Sandoz Products
Sandoz Aluminum Bordeaux 2R	Sandoz Products

TABLE 1 (continued)

DYE	SOURCE
Eastone Red B	Eastman Chemical
Eastone Orange 3R	Eastman Chemical
Eastone Violet BGF	Eastman Chemical
Eastman Orange Green Conc.	Eastman Chemical
Eastone Yellow 5G Conc.	Eastman Chemical
Eastman Black SN	Eastman Chemical
Eastman Fast Yellow GLF	Eastman Chemical

TABLE 1 (Continued)

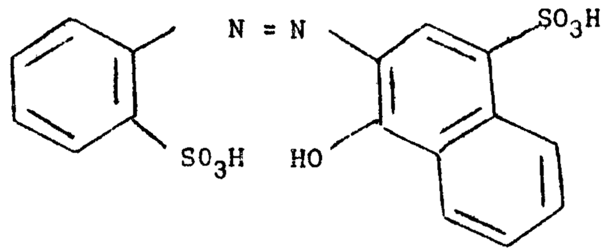
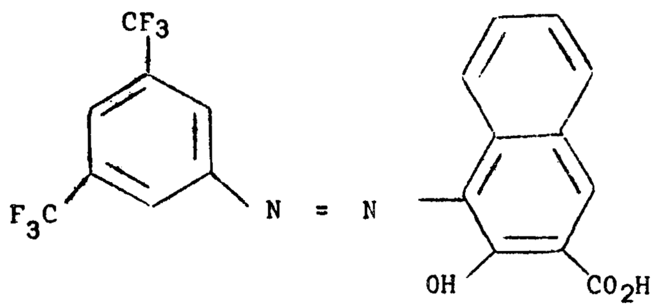
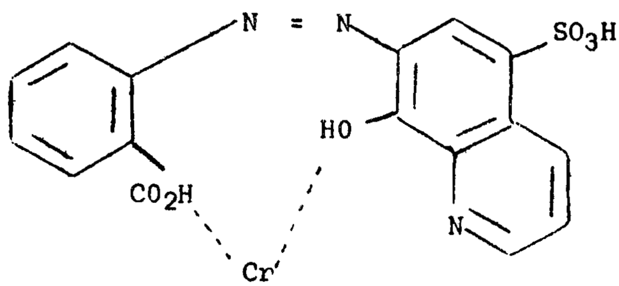
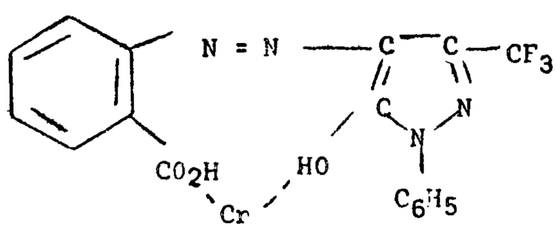
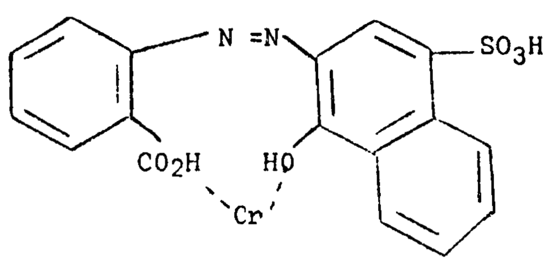
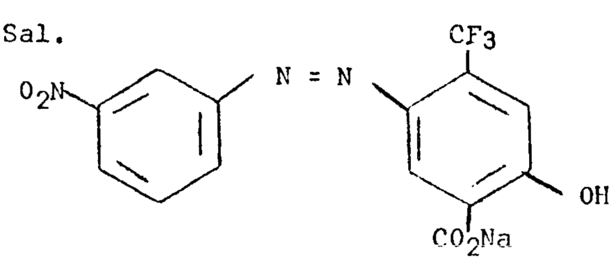
DYE	FORMULA	SOURCE
Temple SN-NW		Temple University
Temple DIF-N		Temple University
Temple AN-SQK		Temple University
Temple AN-FMPK		Temple University
Temple AN-NWK		Temple University
Temple MN-F Sal.		Temple University

TABLE 1 (Continued)

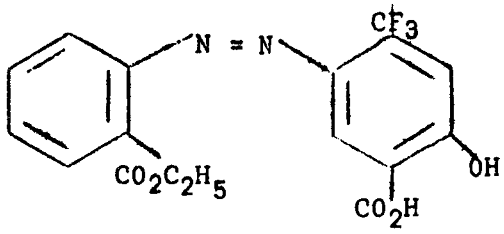
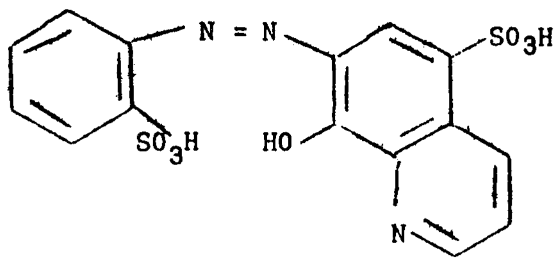
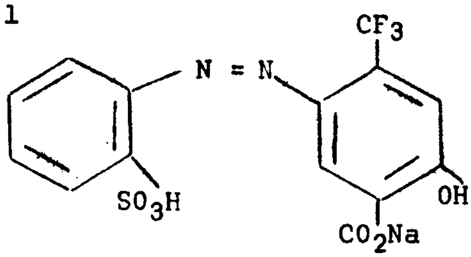
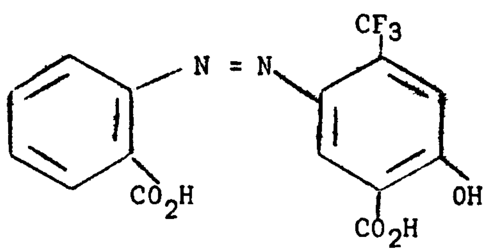
DYE	FORMULA	SOURCE
Temple EA-F Sal.		Temple University
Temple SN-SQ		Temple University
Temple SN-F Sal. 1		Temple University
Temple AN-F Sal.		Temple University

TABLE II

DYES SOLUBLE IN $TiCl_4$

PRODUCER	DYE	COLOR OF SOLUTION
1	Cekyryl Yellow RFC	Yellow-brown
1	Supernylite Brilliant Green B	Green
1	Altocryl Brilliant Red 2R	Red-brown
1	Altocryl Brilliant Red BB	Red-brown
2	Amoplast Pink FFT	Pink-red
2	1, 2 Dihydroxyanthraquinone	Yellow
2	Amenoanthraquinone	Pink
3	Eastone Orange 3R	Orange
3	Eastone Violet BGF	Blue

Producer #1 - Althouse Chemical Company

Producer #2 - American Aniline Products

Producer #3 - Eastman Chemical Company

REACTION OF ORGANIC SOLVENTS WITH $TiCl_4$

It was noticed when $TiCl_4$ was added to certain organic solvents, a dense yellow smoke formed. An experiment was performed wherein $TiCl_4$ was slowly poured into a flask of acetic acid. A dense yellow smoke formed in the flask and "puffed" out the neck. However, as this smoke mixed with and dissipated into the atmosphere, the color disappeared and the normal white smoke appeared. The reaction of $TiCl_4$ with acetone and several members of the ketone series was similar. Several spray systems were constructed in an attempt to intensify the yellow smoke and prolong its life.

The spray systems consisted of the usual nozzles, but instead of discharging directly into the atmosphere, the intermixing sprays were directed into a chamber. The chamber was a 2-1/2" pipe closed at one end, the sprays entered axially. This system did not improve the coloring characteristics of the material, although it was noticed that a colored liquid ran out of the open end of the pipe during smoke formation.

The following materials were reacted with $TiCl_4$ in flasks:

(a) Acetic acid - yellow smoke

(b) Ethyl alcohol - white smoke

(c) Methyl alcohol - white smoke

(d) Anhydrous ether - yellow smoke but not as dense as (a)

(e) Acetone - dense yellow smoke

Various soluble dyes were added to the above materials but did not improve the coloring characteristics.

Indications at this time pointed to the fact that the yellow color was due to the intermediate Ti^{++} complexes and that the absence of water vapor in the air, or partial vacuum conditions might allow the color to persist for a longer period of time.

REACTIONS OF $POCl_3$ AND PCl_3

$POCl_3$ and PCl_3 were first tested in a laboratory hood, being placed in an open beaker. They evolved a tenuous white smoke but much less intense than $TiCl_4$ under the same conditions. Water was added to the beakers and a dense smoke evolved, but not comparable to $TiCl_4$.

Only when a strong ammonia solution was added to PCl_3 did a smoke comparable to the $TiCl_4$-water system evolve. The $POCl_3$-ammonia system did not produce a smoke comparable to the $TiCl_4$-water system.

Dyes soluble in PCl_3 or ammonia or both were added to these materials. The materials were then sprayed together in the usual fashion. The smoke remained white. In efforts to "overpower" the "whiteness" of the smoke, several tests were made with a third container of water-dye solution or ammonia-dye solution spraying into the double stream. The smoke remained white.

The same systems were tested in the steel pipe reactor with negative results.

A further refinement of the reactor was developed. A steel tube 7 inches in diameter by 24 inches long was closed at one end with a hole in the closure. A centrifugal blower was placed in the hole. The PCl_3 was placed in a tray, see Figure 1. The ammonia-dye spray nozzle entered the cylinder directly above the PCl_3 tray. The ammonia dye was sprayed into the PCl_3 and the blower removed smoke as quickly as it was formed. No color other than white was visible in the smoke. The idea of this experiment as opposed to the double spray system was that in the case of droplets mixing, the heat of reaction was dissipated too quickly because of the high area to volume ratio of the droplet. The tray of liquid, on the other hand, would have a relatively low area to volume ratio and if a higher temperature reaction would put dye into the smoke it could be easily observed. Such was not the case. The smoke remained white.

At this point in the work, the staff decided that the coloring of the smoke by means of dyes or other coloring agents was virtually impossible. This decision was also arrived at by the dye companies cooperating with us.

It was decided to explore the possibility of reaction of $TiCl_4$ with an organic compound in the hope of producing a colored reaction product other than those found in the $TiCl_4$-H_2O reaction. Dyes are listed in Table III.

TABLE III

DYES SOLUBLE IN NH_4OH

PRODUCER	DYE	COLOR
1	Azoanthrene Black NV	Black
1	Sol-Aqua-Fast Red 2 BL	Pink
1	Azoanthrene Royal Blue Sconc	Pink
1	Azoanthrene Black WAN	Black
1	Ceksyl Red BB	Red

DYES SOLUBLE IN PCl_3

PRODUCER	DYE	COLOR
1	Experimental Dye 30766A	Red

TESTS AT SIMULATED ALTITUDE AND HUMIDITY

The possibility of colored reaction products was briefly explored under Reaction of Organic Solvents with $TiCl_4$. The work was temporarily suspended for two reasons:

(1) inability of the color to persist beyond the confines of the beaker

(2) the more immediate problem of remaining dye types to be tested

From experiments performed in that phase, it seemed that there was a possibility that the water vapor in the atmosphere was a controlling reaction and any intermediate products would quickly convert to oxides of titanium and hydrochloric acid.

The first experiments performed in this series of tests were conducted in a 5 liter vacuum flask evacuated to 50 microns. 2 cc of $TiCl_4$ were admitted to the flask. Due to the absence of water vapor, no smoke formed. 2 cc of acetone were then admitted into the flask and a light yellow smoke formed immediately and persisted for approximately 10 minutes, slowly turning white. Since the materials were not sprayed into each other, but rather one allowed to flow into the other, a pool of yellow transparent liquid was in evidence at the bottom of the flask. The experiment was repeated several times. It was noted that the admission of air and water vapor caused the smoke to lose the yellow color.

Various soluble dyes were added to the liquids. The yellow color was not affected. It was no deeper nor did it disappear more quickly than without dye.

It was obvious that continuation of the testing in a 5 liter flask would produce qualitative results rather than quantitative. A device for measuring the total obscuring power (TOP) of a smoke was developed.

TOP is a standard measure of smoke intensity used in chemical warfare work, and is defined as the area of smoke produced per pound of material such that the thickness and density of the smoke will obscure a 40 watt light.

A 500 cubic foot vacuum vessel located at the Research Institute Test Site was selected as the reaction chamber.

The experimental apparatus is shown in Figure 2. The area through section A - A^1 is 110 ft.^{2}. The wattage of the tungsten band lamp was set by a variable transformer.

A typical trace from the recorder is shown in Figure 3.

(1) tank clear, no smoke, light out

(2) tank clear, no smoke, light on

(3) tank filled with smoke, light on

V_S is the light picked up through the clear tank

V_O is the light picked up through the smoke filled tank

$V_S - V_O$ is the light obscured

When $V_O = 0$ or $(V_S - V_O)/V_S = 1$, the conditions of TOP have been met.

During an experiment it is impossible, once the light is completely obscured, to show that the particular amount of smoke-producing material was not more than enough to obscure the light completely. Hence, any values of $(V_S - V_O)/V_S = 1$ are ignored and only values of $(V_S - V_O)/V_S$ less than 1 are considered. When plotted on semilog paper as shown in Fig. 7

through 12, the value needed for the TOP computation is found by extrapolating the $(V_S-V_O)/V_S$ line to a value of 1.0.

Since TOP can be defined as Area/pound of material at conditions of TOP, it can be rewritten:

$$TOP = \frac{110 \text{ ft.}^2}{x \text{ pounds of material}}$$

In order to compare the actual numbers and standardize the system, the TOP of the $TiCl_4$-water system was determined.

Figure 7 indicates for TOP conditions, $(V_S-V_O)/V_S = 1$, a volume of 17.5 cc of $TiCl_4$ corresponding to 30.2 g of $TiCl_4$ hence:

$$TOP = \frac{110 \text{ ft.}^2}{30.2/454} = 1640$$

The TOP according to various NASA publications for this system is 1900.

The following systems were tested for TOP in the 500 ft.^{3} vacuum tank at a simulated altitude of 60,000 feet:

SYSTEM	TOP	FIGURE
$TiCl_4$-water	1640	7
$TiCl_4$-acetone	1640	8
$TiCl_4$-diacetyl	1345	9
$TiCl_4$-methyl-ethyl ketone	1410	10
$TiCl_4$-methyl-isobutyl ketone	1030	11
$TiCl_4$-acetic acid	1570	12

It can be seen from the preceding table that the TOP of the $TiCl_4$-water system is equalled by the $TiCl_4$-acetone system and that the $TiCl_4$-acetic acid system compares not unfavorably.

TOP gives no indication of the color of the smoke. This will be discussed in the following section.

MEASUREMENT OF RELATIVE COLOR OF $TiCl_4$ SMOKES USING REACTANTS

It was of interest to determine the relative amounts of red, yellow and green light, both absorbed and reflected, of $TiCl_4$ smokes utilizing water, acetone, acetic acid and alcohol as reactants. The apparatus used in these experiments is shown in Figure 4. It consisted of a 931 A photomultiplier detector coupled with three filters - red, yellow and green - and read out on an oscilloscope. The filter transmission is shown graphically in Figure 5, together with the sensitivity of the 931 A photomultiplier. The three filters were mounted on a revolving plate (60 RPM) enclosed in a light-proof housing. The plate also had an opening with no filter to measure total light.

Figure 6 shows schematically the set-up for the 6' path and the reflected light methods. In the first scheme a 40 watt bulb was placed in the center of one of the sight windows of the 500 ft^3 vacuum tank and the detector was placed directly opposite the bulb at another sight window. The distance between the bulb and the detector was approximately 6'. The materials were injected perpendicularly to the bulb-detector path and the data taken for several minutes after injection. In the second scheme, the detector was placed as close as possible to the sight window and a 700 watt lamp with a reflector was placed at a point where the light produced could be directed through the sight window without being detected by the photomultiplier tube. When the materials were injected perpendicularly to the detector, the reflected light was measured by the photomultiplier tube using the red, yellow, and green filters and no filter.

The data obtained from the preceding experiments are tabulated in Table IV and presented as ratio of red to white, yellow to white and green to white light. Also each value is normalized by dividing each value by the value for the $TiCl_4$-water system. This normalization assumes the $TiCl_4$-water system to be white in both "reflection" and "transmission" (6' path) or both back-scattering and forward-scattering which compensates for the differing filter transmissivities and photocell sensitivities for the three colors.

The normalized reflective data given on Table IV shows that all of the smokes produced are essentially white on reflection since there is neither reduction of the green-white ratio or enhancement of the red-white ratio.

The normalized transmission data (6' path) shows quite clearly that there is a strong coloring of the light transmitted through the three systems investigated. Since TOP of the three systems were all approximately the same (see page 17) to that of the $TiCl_4$-water system, it can be inferred that there must be increased amounts of red and decreased amounts of green light transmitted through these smokes as compared to the $TiCl_4$-water smoke. Table IV shows a relatively large decrease in the green-white ratio supporting the above interpretation.

From these data it is concluded that the experimental smokes, $TiCl_4$ + acetone, $TiCl_4$ + acetic acid and $TiCl_4$ + alcohol show enhancement of the red transmitted light and thus would produce a colored smoke.

TABLE IV

REFLECTIVE System	RED: Red/White	RED: System[a] Water	YELLOW: Yellow/White	YELLOW: System[a] Water	GREEN: Green/White	GREEN: System[a] Water
Water	0.460	1.00	0.440	1.00	0.304	1.00
Acetone	0.372	0.81	0.358	0.81	0.248	0.81
	0.396	0.86	0.385	0.87	0.221	0.73
Acetic Acid	0.420	0.91	0.402	0.91	0.273	0.90
Alcohol	0.468	1.02	0.450	1.02	0.306	1.01
6' PATH						
Water	0.523	1.00	0.504	1.00	0.418	1.00
Acetone	0.580	1.11	0.480	0.95	0.261	0.62
	0.500	0.96	0.415	0.82	0.195	0.47
Acetic Acid	0.533	1.02	0.345	0.68	0.125	0.30
Alcohol	0.527	1.00	0.381	0.76	0.155	0.37

a) Relative value assuming the $TiCl_4$-H_2O system = 1

CONCLUSION AND RECOMMENDATIONS

The survey of dyes that was conducted on this program to color $TiCl_4$ smoke was unsuccessful as very few dyes were found to be soluble in $TiCl_4$ and those that were did not appreciably color the smoke. It is concluded that coloring $TiCl_4$ smoke by soluble dye is presently not feasible.

The use of a two-component system, such as acetone-$TiCl_4$ and acetic acid-$TiCl_4$, shows some promise of producing a yellow colored smoke. The data taken on this program using these dual systems show that a yellow smoke can be produced but its color persistence is not known or completely understood. It would seem that the only way to determine if one of the above systems is feasible for use as a colored smoke trail, is to actually "fly" a pay load utilizing one of these systems. It is suggested that consideration be given to the possibility of just such a flight in the future to determine if the desired colored smoke trail can in fact be produced and if it would persist for an adequate time for experimental wind shear measurements.

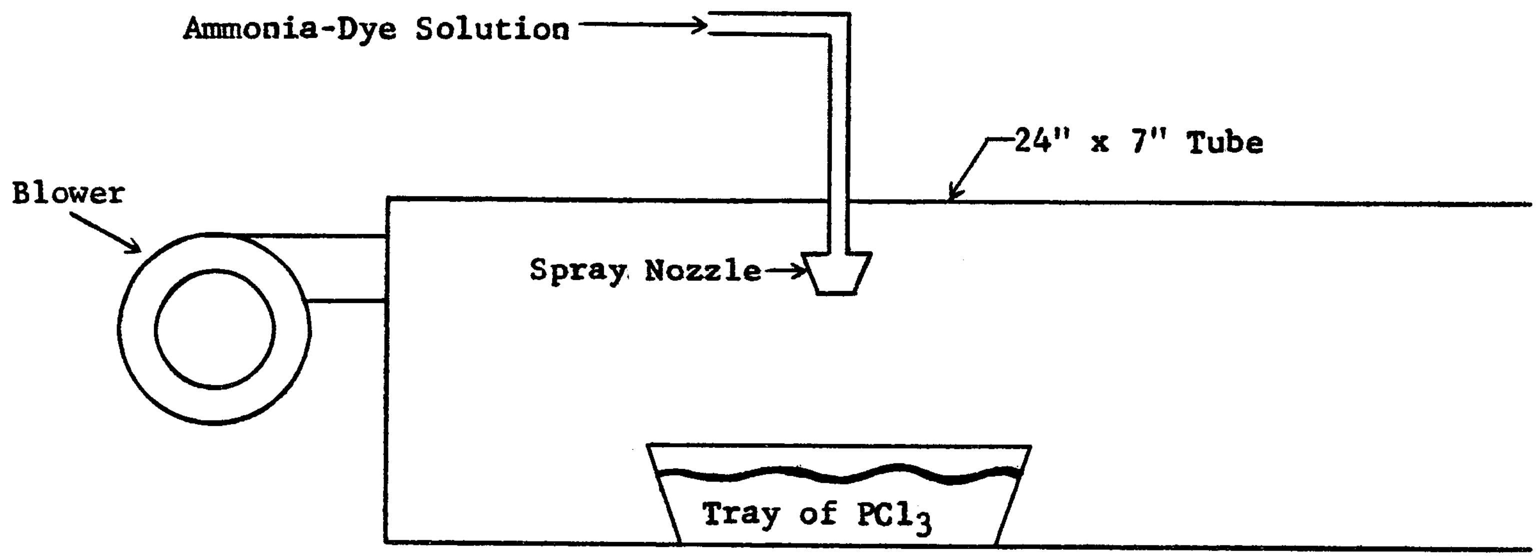


FIGURE 1 - Spray System

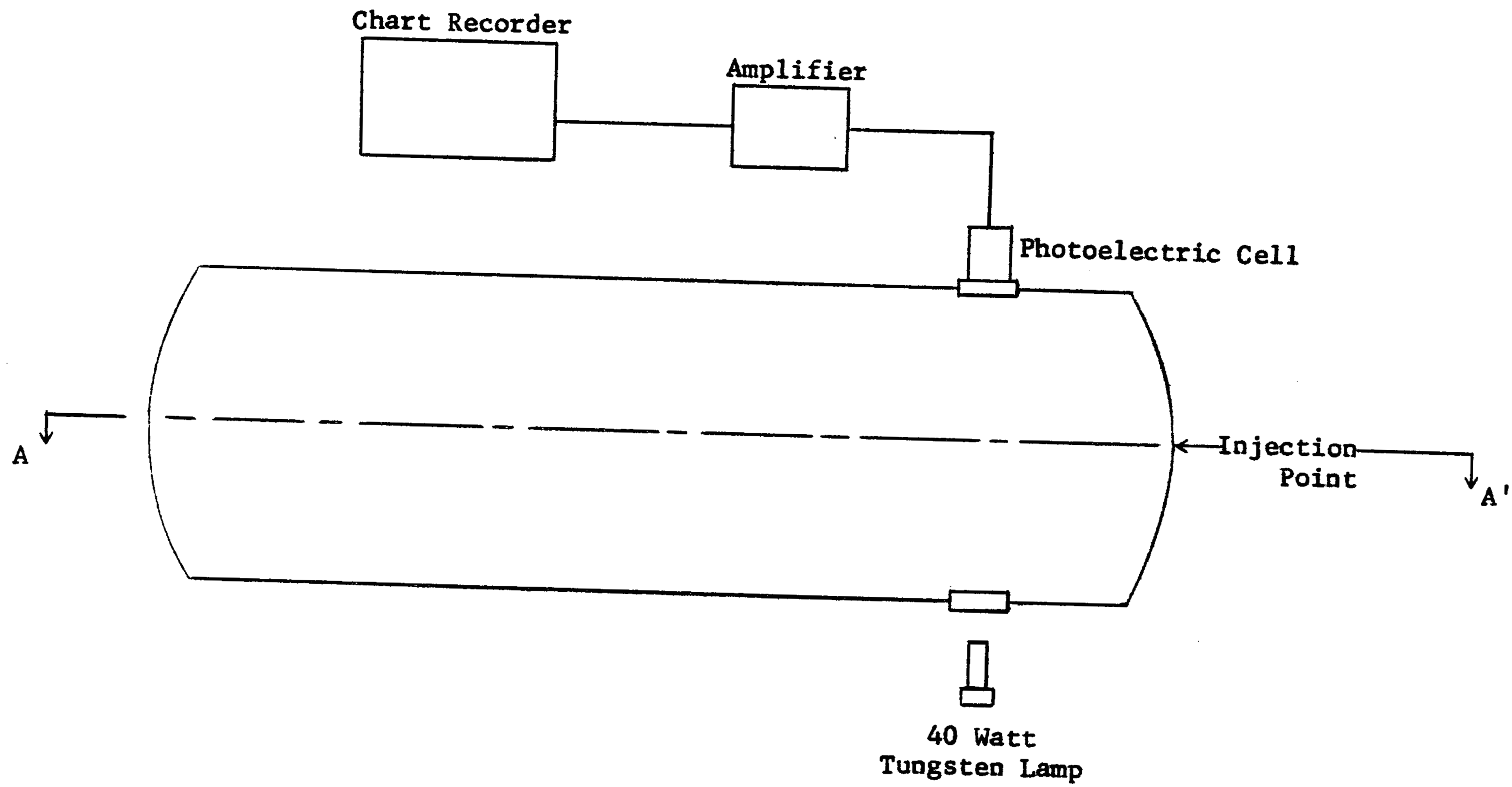
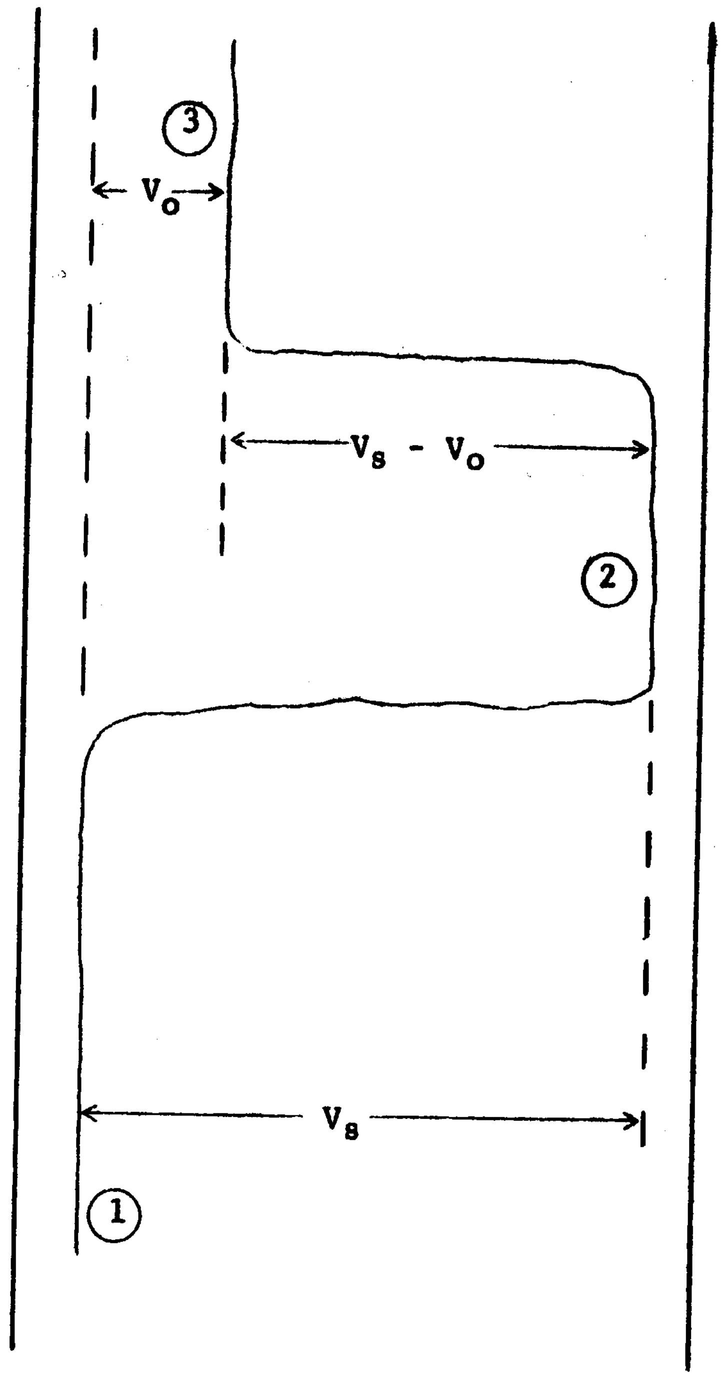


FIGURE 2 - 500 Cubic Foot Vacuum Tank



1 - Tank clear, no smoke, light out
2 - Tank clear, no smoke, light on
3 - Tank filled with smoke, light on

FIGURE 3 - Typical Recorder Tracing

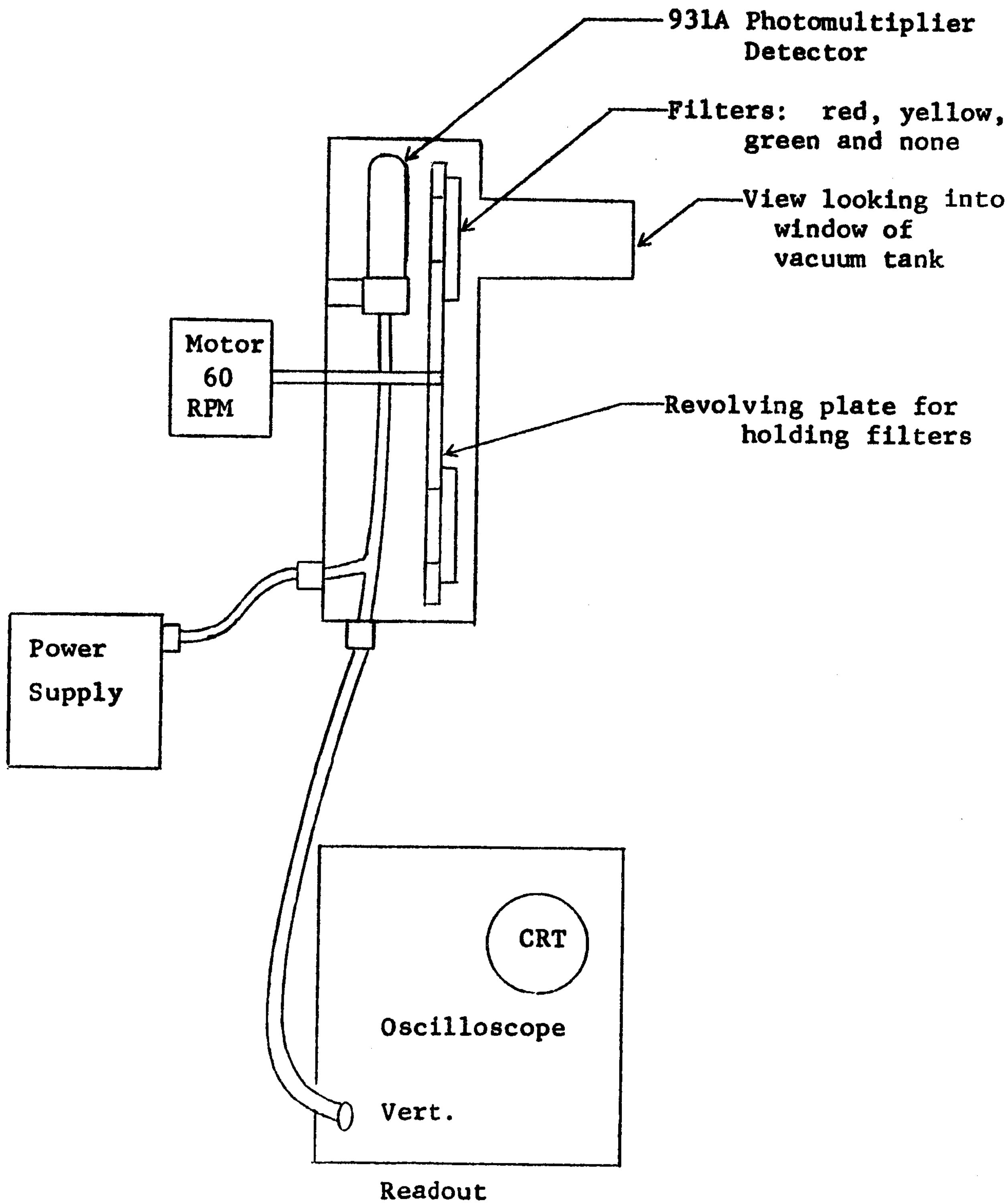


FIGURE 4 - Experimental Apparatus

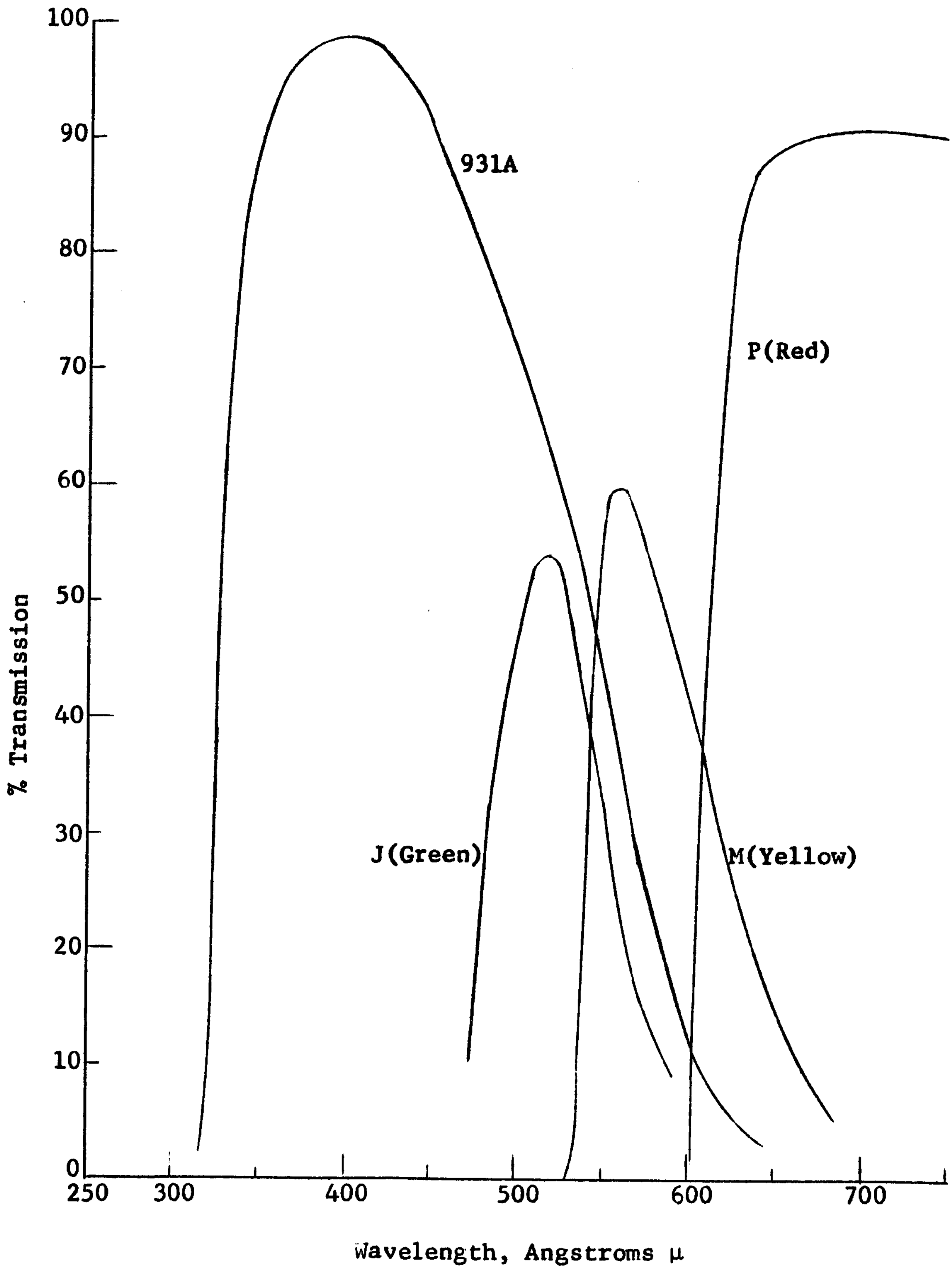
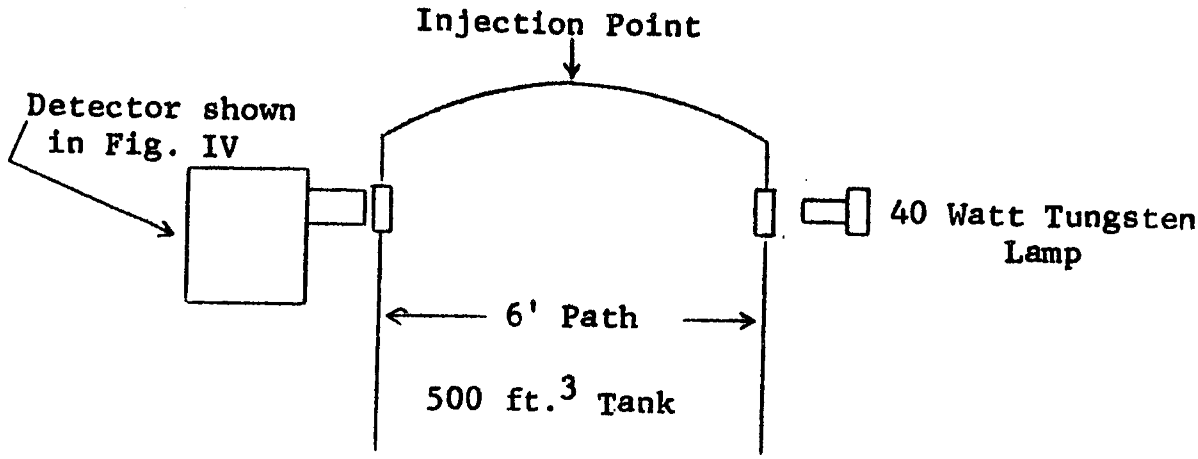
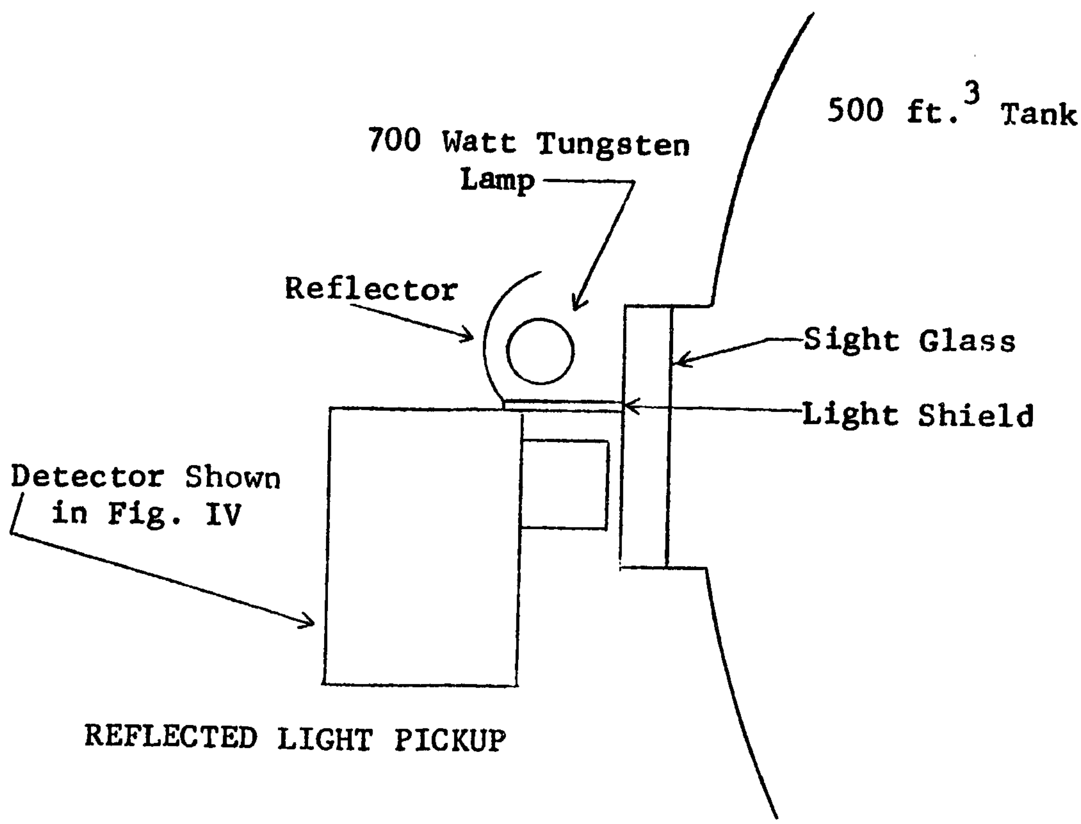


FIGURE 5 - Wavelength vs. Percent Transmission



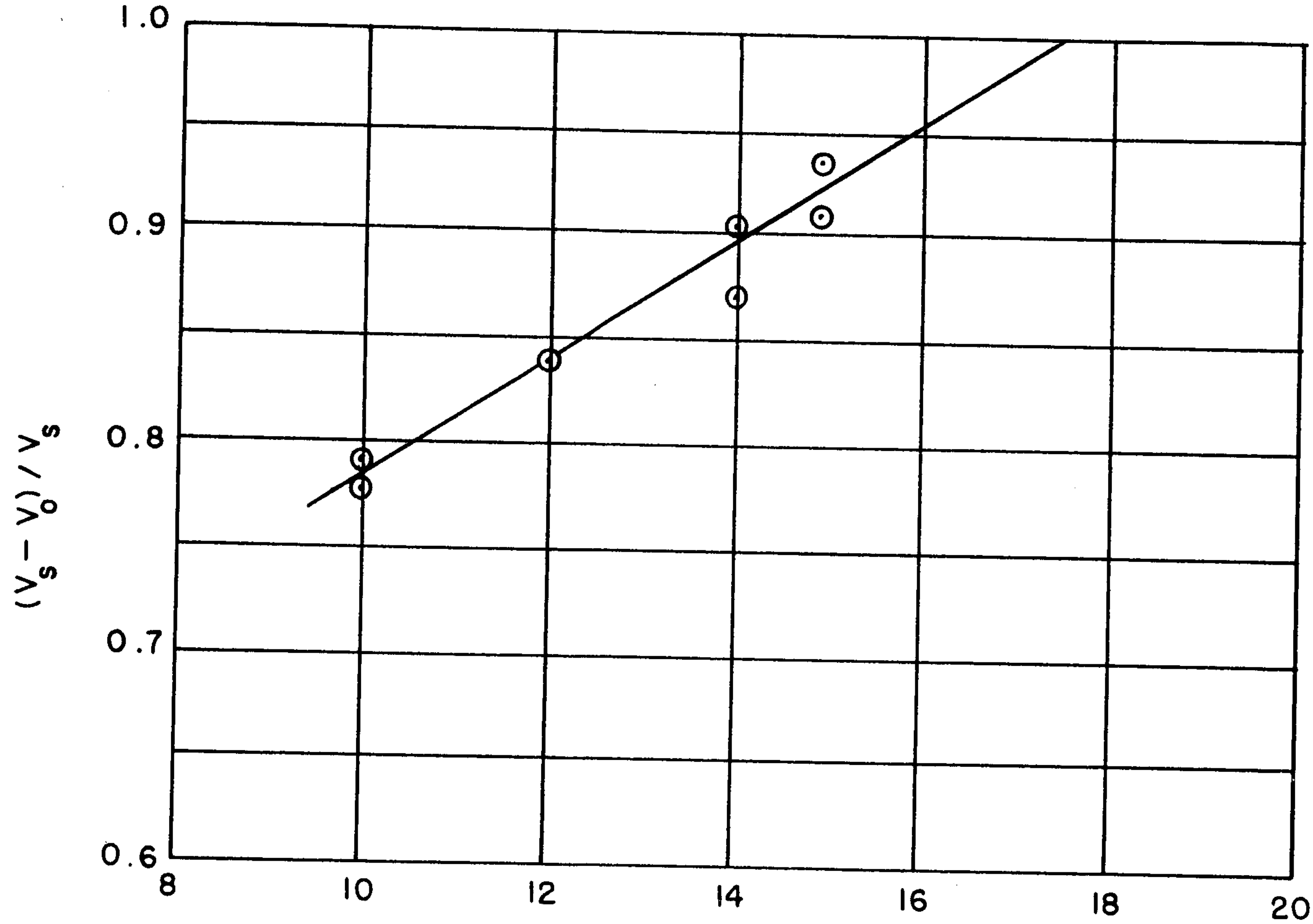
6' PATH PICKUP



REFLECTED LIGHT PICKUP

FIGURE 6

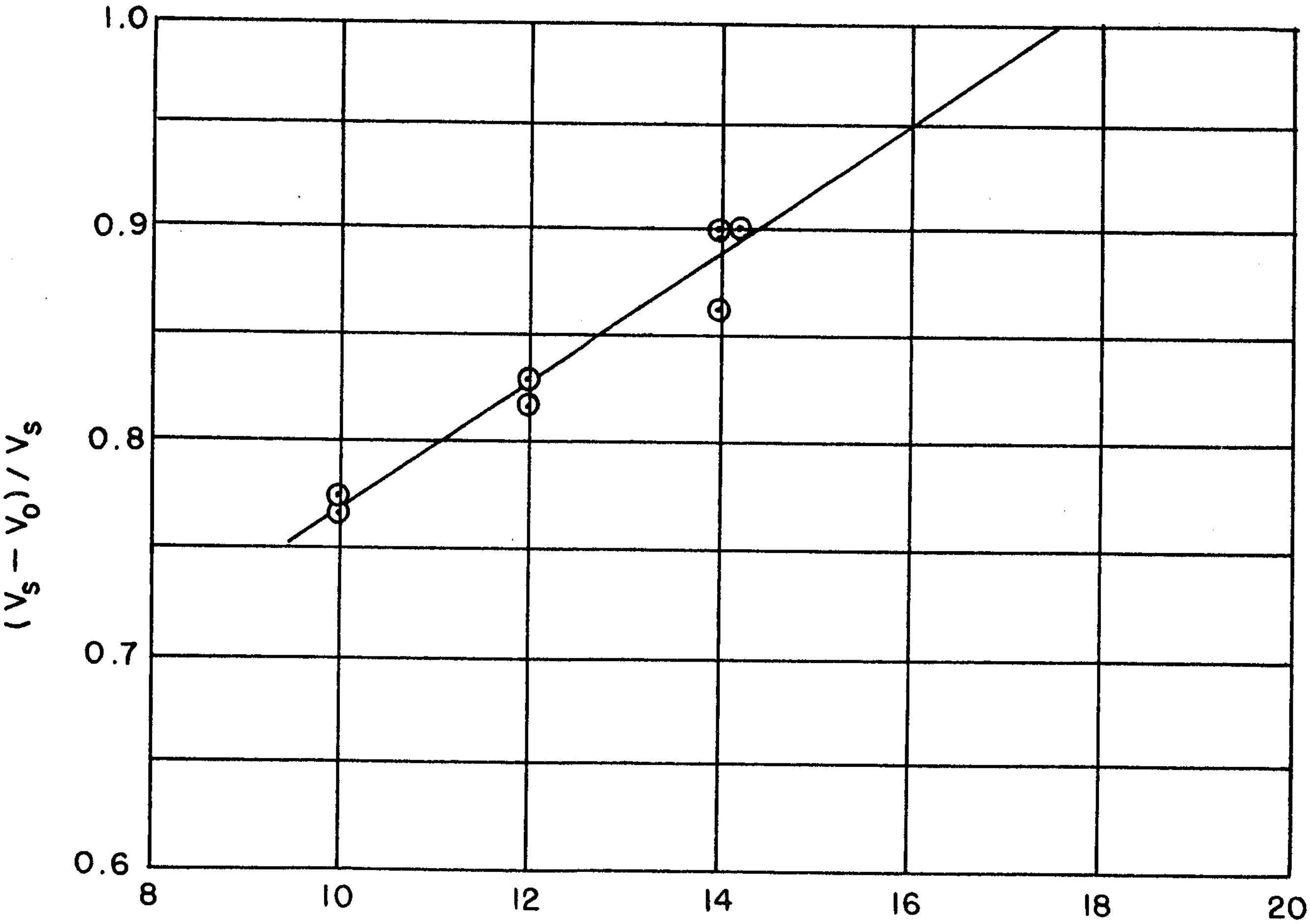
$TiCl_4$ + Water



cc, $TiCl_4$

FIGURE 7

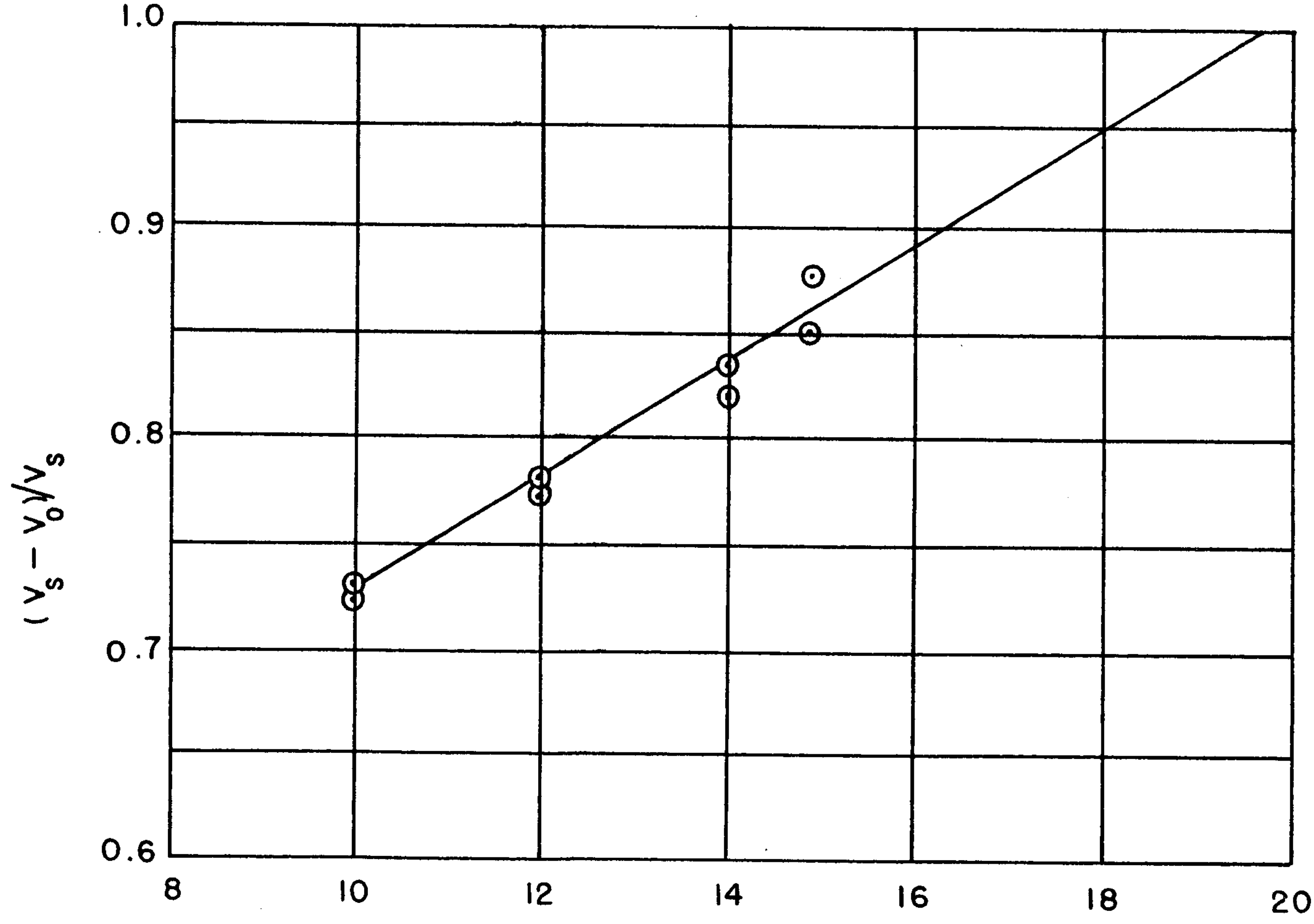
$TiCl_4$ + Acetone



cc, $TiCl_4$

FIGURE 8

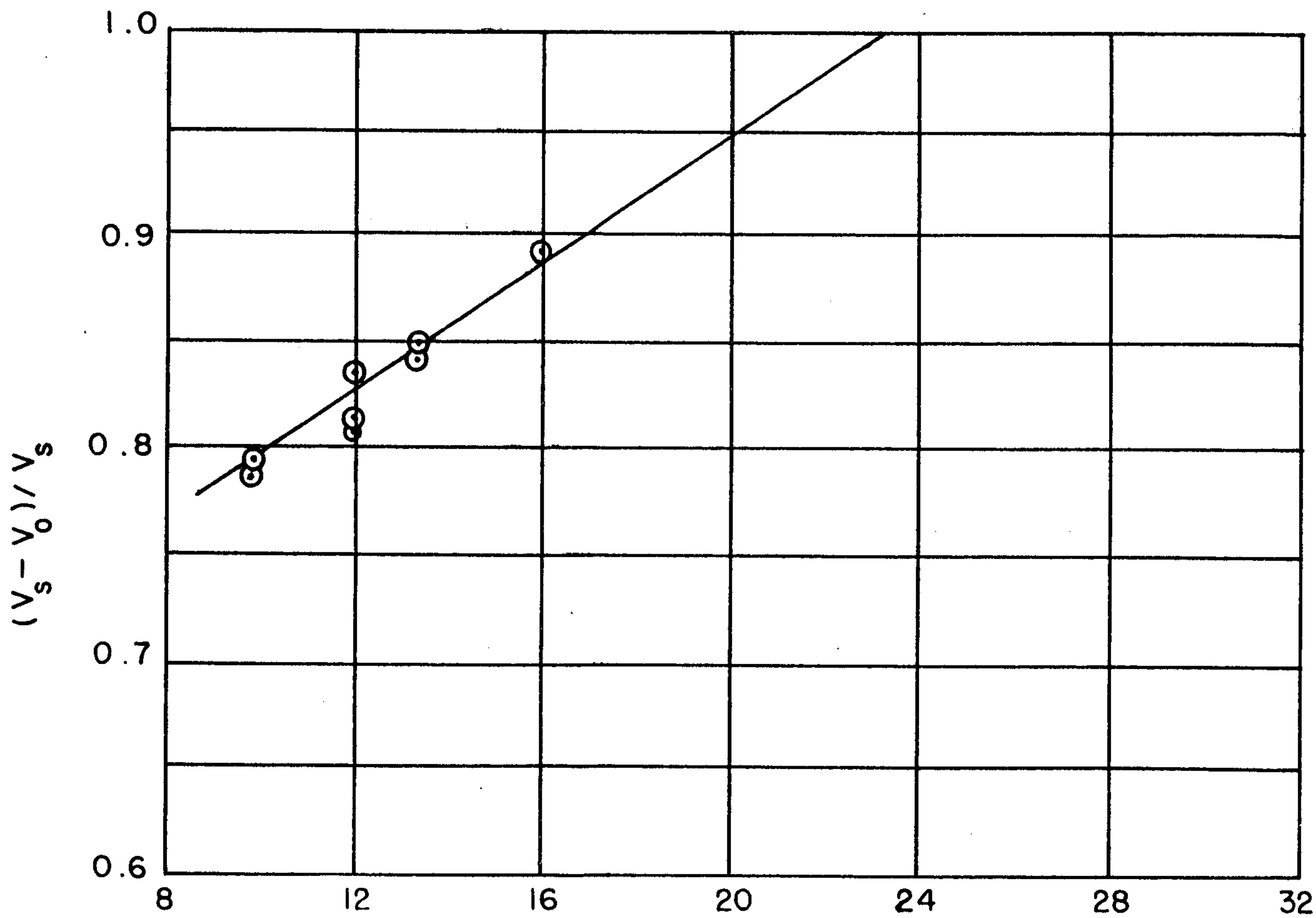
$TiCl_4$ + Diacetyl



cc, $TiCl_4$

FIGURE 9

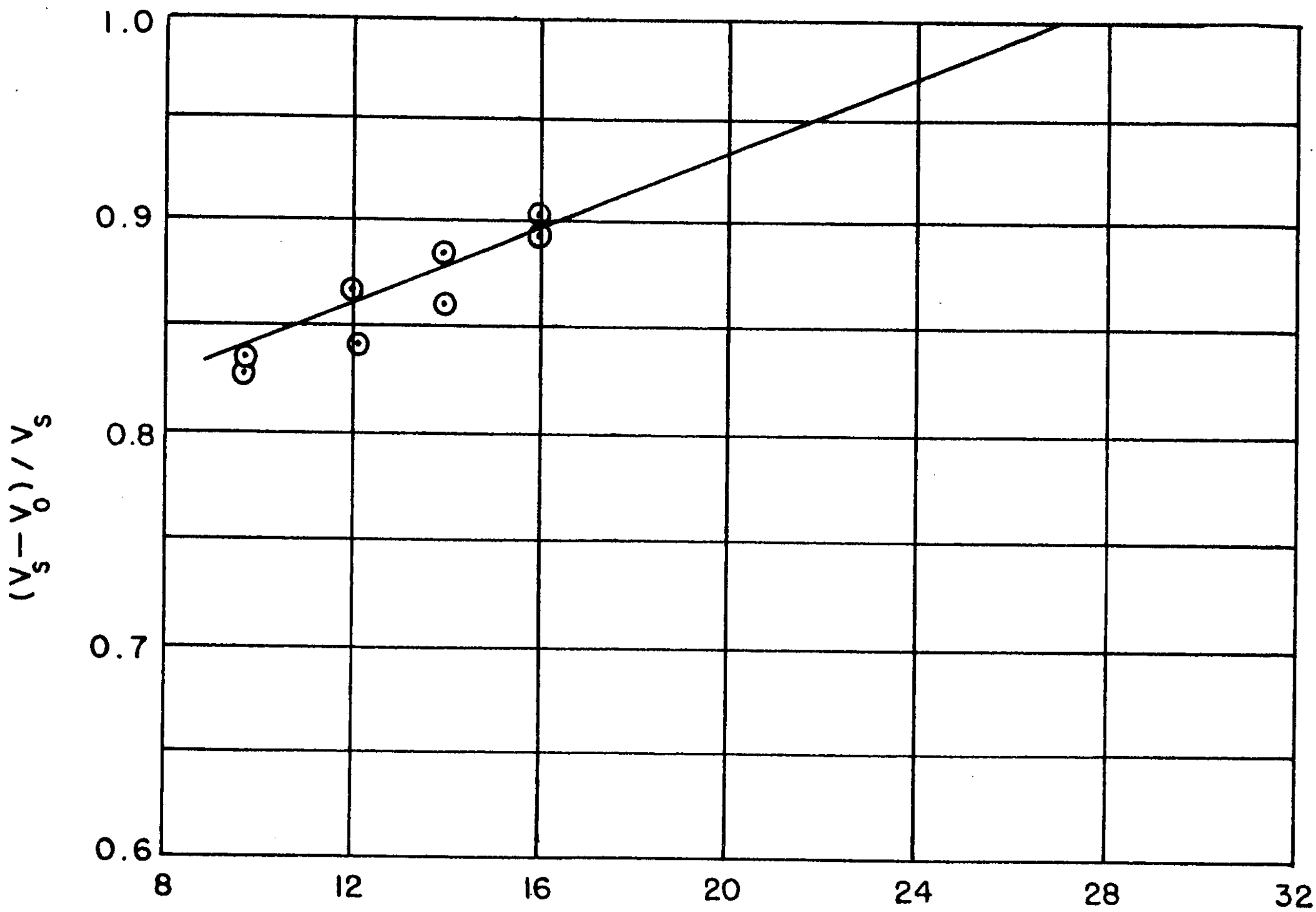
$TiCl_4$ + Methyl Ethyl Ketone



cc, $TiCl_4$

FIGURE 10

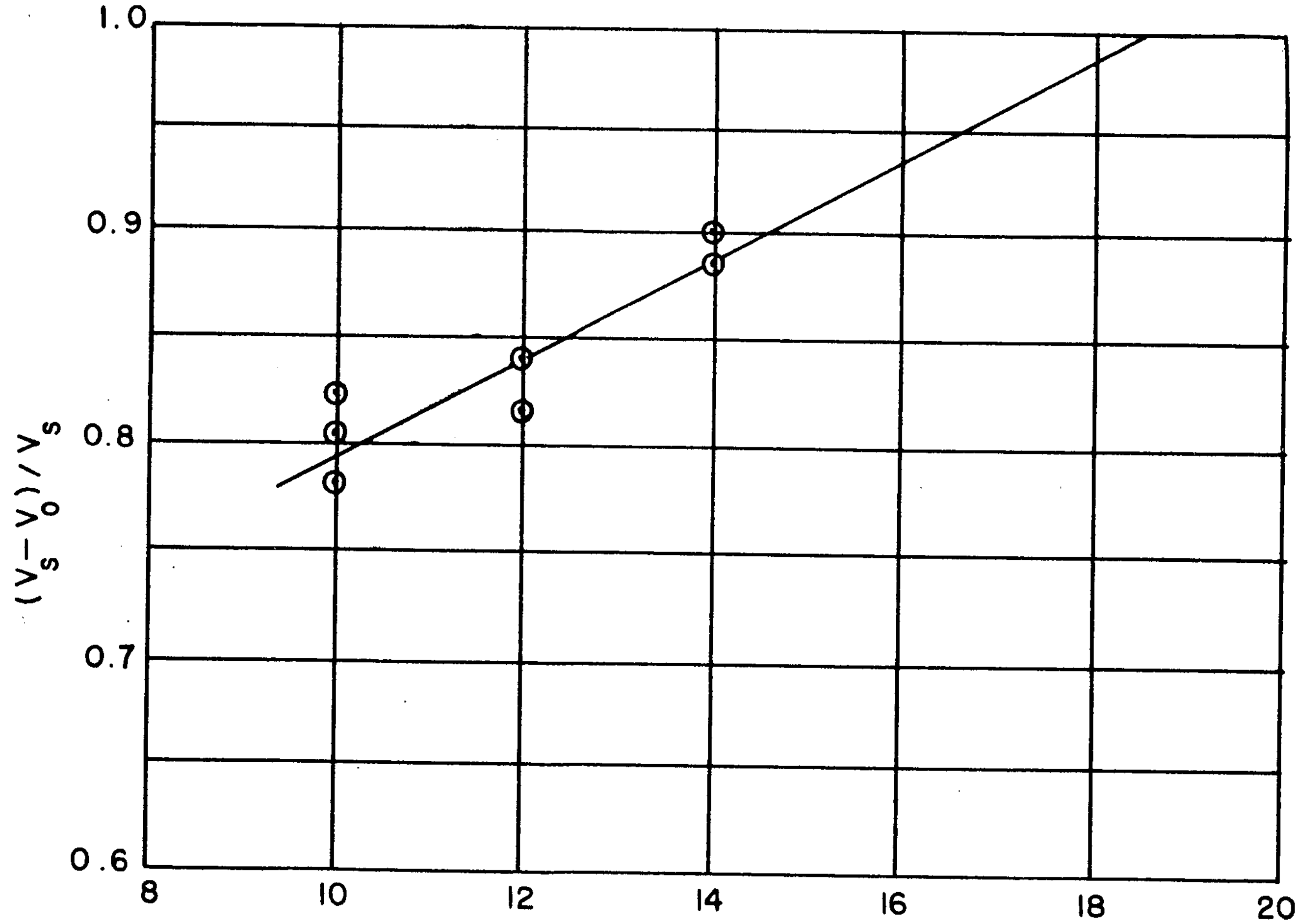
$TiCl_4$ + Methyl Isobutyl Ketone



cc, $TiCl_4$

FIGURE 11

$TiCl_4$ + Acetic Acid



cc, $TiCl_4$

FIGURE 12